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COMPOSITE POWDERS OF THE TiC – TiB<sub>2</sub> SYSTEMI. E. Degraev<sup>1</sup> and Yu. P. Udalov<sup>1</sup>Translated from *Steklo i Keramika*, No. 11, pp. 27–29, November, 2000.

The conditions and parameters of the laboratory synthesis of composite powders of the TiC – TiB<sub>2</sub> system using high-frequency melting are considered and interpreted. The main technological parameters of the synthesis are given.

It is currently necessary to develop new composite materials capable of satisfying requirements imposed by state-of-the-art technology. The development and implementation of technology for producing composite powders based on TiC – TiB<sub>2</sub> will make it possible to replace scarce and expensive tungsten carbide used in certain metal ceramic products. The traditional methods of preparing initial composite powders from presynthesized disperse (or, better still, ultradisperse) titanium boride and titanium carbide powders are expensive, and the materials are not always available. It was previously [1] shown that submicron composite powders of oxygen-free high-melting compounds can be produced from mixtures of the corresponding oxides by parallel carbo-thermic reactions under high-frequency heating. The main problems with respect to this method are related to the selection of the crucible, the type of reducing agent, and the methods mixing of the initial mixture.

We investigated the applicability of several carbonaceous reducing agents, namely, carbon black, natural gas, and saccharose, to solving the specified problems.

In experiments in which carbon black and natural gas were used as the reducing agent, the initial components taken in a certain ratio (the batch compositions are listed in Table 1) were loaded for milling into a vibration grinder with rubber pockets, in order to obtain a homogeneous mixture. The milling bodies in the vibration grinder were hard-alloy

balls whose amount did not exceed 30% of the tray charge. The milling lasted 1 h.

In experiments in which saccharose was used as the reducing agent, the initial components taken in a certain ratio (the batch compositions are listed in Table 2) were loaded, in order to obtain a homogeneous mixture, into a metal beaker and it was filled with distilled water (the weight of the water was equal to the weight of the initial charge). Next, the beaker with the initial mixture was heated on an electric hot plate with periodic stirring of the solution (every 120 sec) up to the end of boiling, when chemically free water was removed.

The criterion for termination of this process was the beginning of thermal decomposition of the saccharose (carbonization of the mixture). Next, the metal beaker with the mixture obtained was placed for 30 min in a muffle located in an exhaust cabinet and heated to a temperature of 500°C, at which thermal decomposition of saccharose and boric acid takes place. Next, the beaker was taken out of the muffle and cooled to the ambient temperature. The mixture obtained was removed from the beaker and ground in a mortar. The experimental production of a composite material of the TiC – TiB<sub>2</sub> system was carried out on an LD2-60 laboratory installation.

The installation is equipped with a high-frequency generator of power 60 kW and frequency 5.28 MHz. The melting was carried out in graphite crucibles of diameters 21 and 45 mm, whose walls had vertical slots (in that way the electric circuit of a “cold” crucible was realized, and all vibrating power was released inside the conducting charge). The crucible loaded with the prepared mixture was placed in a quartz

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TABLE 1

Mixture	Weight content, %		
	TiO <sub>2</sub>	C	B <sub>2</sub> O <sub>3</sub>
1	50.17	29.57	20.26
2	45.50	26.82	27.68
3	61.74	10.00	28.26

TABLE 2

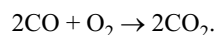
Mixture	Weight content, %		
	TiO <sub>2</sub>	saccharose	H <sub>3</sub> BO <sub>3</sub>
1	27.67	52.50	19.83
2	26.47	50.24	23.29

sleeve located in the field of a water-cooled copper induction heater 100 mm in diameter. The crucible was fixed on a gas-conducting pipe.

In the course of synthesis, the temperature at the end and bottom of the crucible was measured using a Promin' optical pyrometer.

To remove oxygen from the system, a mixture of argon with a carbon tetrachloride additive as the reduction process activator was supplied via the gas-conducting pipe. The conditions of synthesis were as follows: discharge power 12 kW, synthesis duration 3 – 20 min. The sintered cakes obtained were studied using the methods of x-ray phase, derivatographic, and microscopic analysis and focused-beam electron microscopy.

When carbon black was used as the reducing agent, the reduction reaction started 1 – 2 min after the power was switched on. The start of the reaction was judged from the gas emission, i.e., from attainment of the temperature at which reduction of TiO<sub>2</sub> begins, and the gases released from the quartz tube are ignited as a result of the reaction



The cake obtained had heterogeneous coloring: light yellow in the middle (the "light-colored" fraction) and a color from light gray to black at the edges (the "dark-colored" fraction). X-ray patterns of both fractions are shown in Fig. 1.

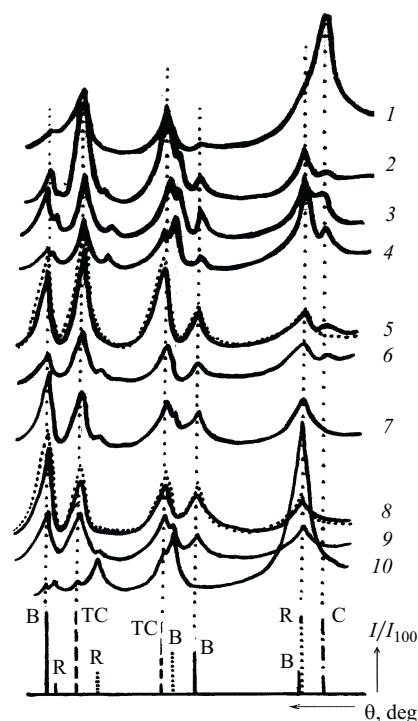
The x-ray phase analysis revealed that the "light-colored" fraction consists mainly of TiO<sub>2</sub> and, to a lesser extent, TiC and TiB<sub>2</sub>, and the "dark" fraction contains a smaller amount of TiO<sub>2</sub>, but larger amounts of TiC, TiB<sub>2</sub>, and carbon.

The nonuniform composition of the product obtained is evidence of the different rates of the reactions at the center and the periphery of the mixture charge, which can be caused by a high temperature gradient across the charge.

When natural gas was used as the reducing agent, natural gas with carbon tetrachloride vapor was supplied to the reaction zone via the gas-conducting pipe during the synthesis. The gas emission in this case was moderate, which points to reduction of the titanium oxide and decomposition of the natural gas. The product obtained had a nonuniform structure: a very strong cake was formed in the lower part, that is, near the crucible bottom, through which the natural gas was supplied (Fig. 1, curve 1). In the upper part the product was unsintered and existed in the form of a powder (Fig. 1, curve 2). The synthesis was conducted for 10 min.

The x-ray phase analysis indicated that the sintered fraction consisted mainly of graphite and, to a lesser extent, TiC and TiB<sub>2</sub>, and the loose fraction contained a larger amount of TiC and smaller amounts of TiB<sub>2</sub> and carbon.

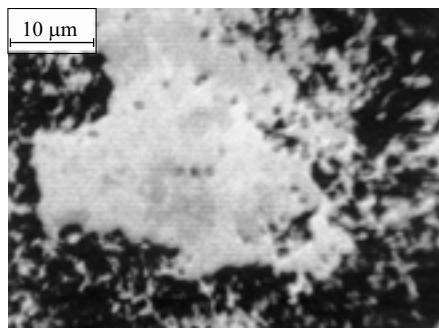
The nonuniform composition of the product obtained is evidence of a high rate of the reaction of decomposition of natural gas in the lower part of the charge, which is caused by the high temperature in the reaction zone. Formation of a compact cake fosters an increase in the hydraulic resistance



**Fig. 1.** X-ray patterns of a composite powder in the TiC – TiB<sub>2</sub> system obtained using various reducing agents: 1) natural gas, lower part of the cake; 2) the same, middle part of the cake; 3) carbon black, reaction duration 15 min, "dark-colored" fraction; 4) the same, "light-colored" fraction; 5) saccharose, the mixture was composed to obtain TiC + TiB<sub>2</sub> with the weight ratio 40 : 60, reaction duration 8 min, dotted curve: after treatment in a glow discharge air plasma; 6) saccharose, reaction duration 5 min; 7) saccharose, TiC : TiB<sub>2</sub> = 60 : 40, reaction duration 5 min (mixture 1); 8) the same, reaction duration 8 min, dotted curved: after treatment in a glow discharge air plasma; 9) the same, reaction duration 5 min (mixture 2); 10) saccharose, TiC : TiB<sub>2</sub> = 60 : 40, reaction duration 3 min; C) graphite (carbon) reflection; R) rutile (TiO<sub>2</sub>) reflection; B) reflection of titanium diboride; TC) reflection of titanium carbide.

of the mixture and a decrease in the amount of gas passing through the reaction zone, which in combination with a large amount of the reactants can lead to a shortage of the reducing agent in the upper part of the charge and, consequently, to a low degree of transformation.

During the synthesis in which saccharose was used as the reducing agent, argon with carbon tetrachloride vapor was supplied to the reaction zone through the gas-feed pipe. Intense gas release was observed in that case, which points to the intensity of the titanium oxide reduction. The treatment duration in synthesis was equal to 10 min for mixture 1, and 3, 5, 8 and 10 min for mixture 2. The products obtained had a homogeneous structure and the grayish-golden color, which points to a certain amount of TiN or TiO impurity. X-ray patterns of the products are given in Fig. 1, curves 5 – 8 (mixture 1) and curves 9, 10 (mixture 2).



**Fig. 2.** Aggregate of a composite powder of the TiC – TiB<sub>2</sub> system. Light-colored area — TiB<sub>2</sub>; dark grains — TiC.

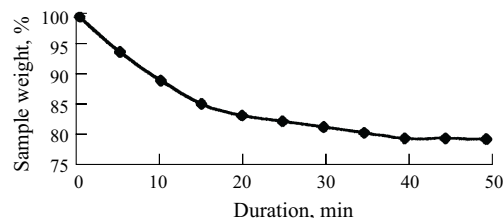
The x-ray phase analysis revealed that the product consists mainly of TiC and TiB<sub>2</sub> and contains a certain amount of TiO<sub>2</sub>. Among the samples, the product obtained from mixture 2 treated for 8 min contains the smallest amount of TiO<sub>2</sub>, which can be related to the beginning of decomposition of the product under the effect of air oxygen.

The microphotographs of a section of a composite-powder grain are shown in Fig. 2. It is possible to see the grain morphology of the composite powder produced from mixture 1 with a synthesis duration of 10 min. The aggregate seen in the photograph consists of submicron particles of TiC (dark grains) in a TiB<sub>2</sub> matrix.

The synthesis that was not accompanied by supply of carbon tetrachloride vapor had weak gas emission (Fig. 1, curves 9 and 10). In this case, the main part of the product is composed of TiO<sub>2</sub>, and the content of TiC and TiB<sub>2</sub> is lower than in the experiments with an additive of carbon tetrachloride vapor, which is evidence of the positive effect of the activating additive of carbon tetrachloride vapor and the advisability of its use.

The product of melting in an induction furnace contains a certain quantity of unbound residual carbon. In the course of manufacture and subsequent service of articles, the residual-carbon impurity has a negative effect and degrades the article properties. Therefore, removal of unbound residual carbon from the material is important. The present study investigated the possibility of implementing such purification in a high-frequency glow discharge, using air as the plasma-forming gas.

During the treatment, air was supplied to the reaction zone through a needle valve, the pressure inside the reactor chamber was maintained at the level of 66.5 Pa, and the vibration frequency was 27.12 MHz. The discharge color changed from a pink shade typical of air plasma to a sky-blue shade typical of plasma containing CO, which points to an intense process of oxidation of carbon-bearing components.



**Fig. 3.** Change in the weight of a composite powder of mixture 1 under treatment in a glow discharge air plasma.

The change in the weight of a powder sample as a function of the duration of the glow discharge treatment in air is shown in Fig. 3.

An analysis of the x-ray patterns of the initial and end products (Fig. 1) shows that the intensity of reflections of TiC and TiB<sub>2</sub> was somewhat increased, which is evidence of the inertness of TiC and TiB<sub>2</sub> to the glow discharge air plasma at a pressure of 66.5 Pa, whereas the blurred reflection in the region of  $\Theta = 12 - 14^\circ$ , which indicates the presence of graphite, disappeared from the pattern, which points to the expediency of such purification in a high-frequency glow discharge using air as the plasma-forming gas.

Thus, the most complete and fastest transformation leading to formation of the product of the required composition takes place, when saccharose is used as the reducing agent. Use of lamp black and natural gas as the reducing agent is ineffective, due to the low reaction rate and the relatively low product yield with high labor consumption and a long batch preparation process.

Introduction of carbon tetrachloride vapor into the reaction space significantly accelerates the reaction rate. For instance, the time needed to complete the reaction, when saccharose is used as the reducing agent, decreases from 10 – 15 to 4 – 6 min.

When air is used as the plasma-forming gas, the pressure inside the reactor being 66.5 Pa, efficient removal of residual free carbon (in the form of oxides) is observed. At the same time, TiC and TiB<sub>2</sub> are not oxidized. With the pressure in the reactor exceeding 66.5 Pa, an increase in the sample weight is observed, which is evidence of oxidation of the material to TiO<sub>2</sub>.

The results obtained can be used for practical purposes.

## REFERENCES

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